1 **METHOD FOR ENHANCING THE RETENTION EFFICIENCY OF**
2 **TREATMENT CHEMICALS IN SUBTERRANEAN FORMATIONS**
3
4 <u>TECHNICAL FIELD</u>
5
6 The present invention relates generally to the treatment of hydrocarbon
7 bearing subterranean formations with chemicals, and more particularly, to
8 those methods which enhance the retention of the treatment chemicals, such
9 as scale inhibitors, in the formations.
10
11 <u>BACKGROUND OF THE INVENTION</u>
12
13 Treatment chemicals are often injected into subterranean formations
14 containing hydrocarbons to aid in the production of the hydrocarbons.
15 Examples of such treatment chemicals include scale inhibitors, corrosion
16 inhibitors, asphaltene inhibitors, gas hydrate formation inhibitors, and wax
17 deposition inhibitors. Ideally, these treatment chemicals will be retained by
18 the subterranean formation with the treatment chemicals slowly being
19 released from the formation and into the production fluids to provide treatment
20 over an extended period of time. The slow release of the treatment chemicals
21 can provide beneficial effects to the subsurface formation and fluid flow
22 therein, to the well bore and to other downstream flow lines and fluid flow.
23
24 As a particular example, scale may cause restriction in flow due to scale
25 deposition in the formation near the well bore, perforations, well bore, flow
26 lines and facilities in hydrocarbon producing systems causing a reduction in
27 the rate of oil and/or gas production. A common method to address scaling
28 problems is to subject the production well to a "squeeze" treatment whereby
29 an aqueous composition comprising scale inhibitors, such as phosphate
30 esters and phosphonates, are introduced into the well, usually under
31 pressure, and "squeezed" or forced into the formation and held there by
32 physical or chemical means. The "squeeze" treatment often needs to be done
33 one or more times a year and constitutes "down time" when no production

1 takes place. Over the year there is a reduction in total production

2 corresponding to the number of down times during the squeeze operations, as

3 well as reduced production as the scaling problem builds up. The net result is

4 frequent well interventions which impact well productivity and field profitability.

5

6 Conventionally, a rule of thirds is used when calculating a squeeze operation

7 for scale inhibitors. Generally, a third of the inhibitor will immediately return

8 when the well is put back on production, a third will be ineffective, and a third

9 will be retained in the formation rock and will be slowly released during the life

10 of the squeeze. Accordingly, a great amount of the scale inhibitor is

11 ineffective, increasing the overall cost of the chemicals needed to do the

12 treatment job. Further, because of the low retention efficiency, the time

13 between treatment jobs is unduly short as well.

14

15 Calcium ions are often involved in the precipitation or adsorption of

16 phosphonates. It currently believed that the phosphonates react with calcium

17 ions to form a condensed phase that separates from a carrier fluid by

18 adsorption or precipitation and is retained in the formation. A serious problem

19 is getting the calcium and scale inhibitor to interact in the right location. If the

20 scale inhibitor and calcium ions are mixed at a well surface, then precipitation

21 may occur prematurely in the well bore. If the scale inhibitor is injected into

22 the formation and followed by a calcium rich slug of fluid, the mixing in the

23 formation can be very inefficient. The calcium slug tends to displace the

24 inhibitor with little intermixing. Acidic inhibitors can often generate calcium

25 ions by dissolving minerals like calcite that are already in the formation.

26 However, this is not always as controlled as desired and in formations where

27 there is little to no calcite, this is not a good option.

28

29 Use of water continuous phases as a carrier for treatment chemicals has

30 shortcomings. Addition of significant amounts of water into a well can, at least

31 temporarily, decrease the permeability of the formation to oil flow. The

32 addition of water may cause clays to swell, again reducing the flow capability

33 of hydrocarbons through a formation. Further, as water is significantly denser

1 than a like volume of oil, low pressure reservoirs may require additional lift

2 support to produce fluids from the hydrocarbon bearing formations.

3

4 Use of a generally oil continuous phase as a carrier for treatment chemicals

5 overcomes some problems associated with using water continuous phases.

6 The preparation of water in oil microemulsions to deploy scale inhibitors is

7 described in U.S. Patent Number 6,581,687 to Collins et al. The disclosure in

8 this patent is hereby incorporated by reference in its entirety. A

9 microemulsion is formed by dispersing an aqueous phase containing a scale

10 inhibitor in an oil phase. The microemulsion is then placed down a production

11 well and into a formation. The formation is then squeezed.

12

13 However, like the use of water continuous phases for delivering treatment

14 chemicals to subterranean formations, the method of Collins et al. results in a

15 substantial portion of the introduced treatment chemicals being flushed back

16 with production fluids rather than being retained by rocks of the formation for a

17 slow release over an extended period of time. More efficient retention of the

18 treatment chemicals would extend the life time between squeezes.

19

20 The present invention addresses the aforementioned shortcomings in prior

21 methods of chemically treating subterranean formations.

22

23   <u>SUMMARY OF THE INVENTION</u>

24

25 A method for retaining a treatment chemical in a subterranean formation

26 containing hydrocarbons is disclosed. The method includes first preparing an

27 emulsion or microemulsion. The emulsion contains an oil continuous phase

28 and first and second aqueous phases. The oil continuous phase preferably

29 includes at least one surfactant which aids in the formation of the oil

30 continuous emulsion. The first aqueous phase includes a treatment chemical.

31 The second aqueous phase comprises a retention enhancing chemical which

32 is to be reacted with the treatment chemical in the subterranean formation.

33 Preferably, the first and second aqueous phases remain generally separately

1   dispersed and stable within the oil continuous phase prior to being introduced

2   into the subterranean formation.

3

4   The emulsion is then placed down a well bore and into the subterranean

5   formation. The first and second aqueous phases then interact with one

6   another in the subterranean formation such that the first treatment chemical

7   and the retention enhancing chemical react with one another resulting in the

8   treatment chemical being retained in the subterranean formation at a greater

9   efficiency than had the second aqueous phase, including the retention

10   enhancing chemical, not been used.

11

12   The oil continuous phase and the first and second aqueous phases may invert

13   or break into a water continuous phase or even into separate oil and aqueous

14   phases within the subterranean formation to enhance the rate of reaction

15   between the treatment chemical and the retention enhancing chemical. The

16   inversion, breaking or separation of the emulsion may be enhanced due to a

17   number of factors. First, the subterranean formation may include sufficient

18   water to assist in the inversion of the emulsion from an oil continuous phase

19   to a water continuous phase. Also, the emulsion may receive heat from the

20   formation which can enhance the inversion process. Salt present in the

21   formation and/or chemicals pre-existing in the formation which can change the

22   pH of the emulsion components may aid in increasing the reaction rate

23   between the treatment chemical and retention enhancing chemical.

24

25   Preferably, the first aqueous phase and the second aqueous phase are

26   prepared as separate oil continuous emulsions prior to their being mixed

27   together to form the oil continuous emulsion which is placed down the well

28   bore and into the subterranean formation. Examples of treatment chemicals

29   include scale inhibitors, corrosion inhibitors, asphaltene inhibitors, gas hydrate

30   inhibitors, wax deposition inhibitors, proppants, and polymer and conformance

31   controllers. Examples of retention enhancing chemicals include Group II

32   metals, Group III metals, transition elements or organic molecules in an

33   amount sufficient to react with the treatment chemical.

1   An object of the present invention is to provide a method in which the

2   retention percentage of a treatment chemical introduced into a subterranean

3   formation is enhanced over conventional deployment methods. Because of

4   the increased retention efficiency of the treatment chemical, less of the

5   treatment chemical may be required to complete a treatment job and/or else

6   the overall time between treatments may be extended.

7

8   It is another object to introduce an emulsion into a subterranean formation

9   which contains an oil continuous phase with a first aqueous phase including a

10   treatment chemical and a second aqueous phase including a retention

11   enhancing chemical which reacts with treatment chemical in the subterranean

12   formation to increase the retention efficiency of the treatment chemical.

13

14   Yet another object is to use conditions existing in a subterranean formation,

15   such as the presence of water, heat, minerals and salinity, to assist in the

16   inversion of an emulsion from an oil continuous phase to a water continuous

17   phase wherein a treatment chemical and retention enhancing chemical are

18   allowed to react to increase the amount of the treatment chemical which will

19   be retained by rocks of the formation.

20

21   <u>BEST MODE(S) FOR CARRYING OUT THE INVENTION</u>

22

23   A method for retaining a treatment chemical in a subterranean formation

24   containing hydrocarbons is disclosed. The method includes first preparing an

25   emulsion or microemulsion. For the purposes of this invention, either an

26   emulsion or microemulsion may be used. The term "emulsion" shall

27   hereinafter refer to both emulsions and microemulsions. The emulsion

28   contains an oil continuous phase and first and second aqueous phases. The

29   first aqueous phase includes a treatment chemical. The second aqueous

30   phase comprises a retention enhancing chemical which is to be reacted with

31   the treatment chemical in the subterranean formation. Preferably, the first

32   and second aqueous phases remain generally separately dispersed and

33   stable within the oil continuous phase prior to being introduced into the

1   subterranean formation. Of course, it will be appreciated that a certain limited

2   amount of mixing and reacting of the aqueous phase will occur during the

3   creation of the emulsion.

4

5   The emulsion is then placed down a well bore and into the subterranean

6   formation where the emulsion will break or invert. The first and second

7   aqueous phases then interact with one another in the subterranean formation

8   such that the first treatment chemical and the retention enhancing chemical

9   react with one another resulting in the treatment chemical being retained in

10 the subterranean formation at a greater efficiency than had the second

11 aqueous phase, including the retention enhancing chemical, not been used.

12

13 Oil external emulsions or microemulsions can be made with a chemical rich

14 aqueous phase. In the present invention, two emulsions may be used. In the

15 first emulsion, a scale inhibitor would be dissolved in the internal water phase.

16 In the second phase, the internal water phase would be rich in calcium or

17 other precipitating ion. Prior to injecting into the well, the two emulsions would

18 be mixed. Since the internal phase droplets are stable and completely

19 surrounded by the oil phase, the two internal phases would not contact and

20 thus not be able to interact. The emulsions are stabilized with a non-ionic

21 surfactant or some combination of surfactants that have a non-ionic

22 component. Non-ionic surfactants exhibit cloud points or phase inversion

23 temperatures. This phase inversion temperature is a temperature at which

24 the non-ionic surfactant becomes more hydrophobic. This temperature

25 change upsets the hydrophile-lypophile balance and the emulsion will break

26 or invert, so that the aqueous phase becomes the external or continuous

27 phase. Since the inhibitor and calcium are both in the aqueous phases, they

28 can now interact and precipitate.

29

30 In practice, the well bore and near formation is cooled and prepared by a

31 preflush, then the mixed emulsion is injected. The well is shut in for 8-24

32 hours, while heat from the reservoir matrix warms the emulsion and inverts it.

33 Alternatively, the inhibitor microemulsion can be displace by a hot post flush.

1 This will quickly reheat the near well bore and force precipitation. Selection of

2 chemical systems that will trigger an inversion at specified temperatures is

3 well known to those versed in the art of scale treatment with scale inhibitors.

4 Phase inversion temperatures can be defined relatively precisely. Alternately,

5 ionic surfactants typically become more hydrophilic with temperature

6 increases and can also be used.

7

8 **I.   Preparation of the Emulsion**

9

10 The emulsion is ideally prepared by blending together a first base oil

11 continuous emulsion containing the first aqueous phase including the

12 treatment chemical and a second base oil continuous emulsion containing a

13 second aqueous phase having the retention enhancing chemical.

14 Alternatively, although not as preferred, the first and second aqueous phases

15 can be directly mixed with an oil phase. The aqueous phases are ideally in

16 the form of small droplets interspersed throughout the continuous oil phases.

17 Emulsions containing the first and second aqueous phases are formulated to

18 allow the aqueous phases of each emulsions to remain separate and stable

19 when blended together yielding the overall emulsion. The emulsion will

20 remain generally stable until being introduced into the subterranean formation

21 wherein the first and second aqueous phases combine.

22

23 **A.   First Base Emulsion Including Treatment Chemical**

24

25 The first base emulsion includes an oil base with surfactants. An aqueous

26 phase containing the treatment chemical, such as a scale inhibitor, is

27 prepared and mixed into the oil base and surfactants.

28

29 **Oil Phase**

30

31 The oil phase can be almost any liquid which is immiscible with the aqueous

32 phase. For example the oil phase may be a paraffin oil, a natural oil, diesel,

33 kerosene, gas oil, crude oil, base oil, may be selected from the group

1 consisting of liquid alkanes (preferably C_5 -C_{20} alkanes, more preferably C_8 to

2 C_{15} alkanes, most preferably C_9-C_{12} alkanes, for example, n-nonane, n-

3 decane, and n-undecane), and liquid aromatic hydrocarbons (for example,

4 toluene and xylene). The most preferred oil to be used for the oil phase is

5 diesel.

6

7 **Surfactant**

8

9 A surfactant is ideally mixed in with the oil prior to the aqueous phase being

10 added. The surfactant helps in the formation of the oil external emulsion.

11 Suitably, the surfactant(s) may be an anionic surfactant or a non-ionic

12 surfactant, i.e. a surfactant having anionic and non-ionic head groups

13 respectively. Examples of anionic head groups include sulfosuccinate, sulfate,

14 phosphate, carboxylate, sulfonate, and other water-soluble groups. Suitable

15 counter-ions to the anionic head groups include sodium, potassium and

16 ammonium cations. Suitable non-ionic head groups include alkoxylate

17 groups. Typically, the surfactant(s) may have one or more hydrocarbon tail

18 groups, for example 1 to 3 hydrocarbon tail groups. The hydrocarbon tail

19 group(s) may be a halogenated hydrocarbon group such as a fluorinated

20 hydrocarbon group. Generally, the hydrocarbon tail group is an alkyl group

21 having a chain length of at least 5 carbon atoms, preferably at least 8 carbon

22 atoms. Preferably, the hydrocarbon tail group is an alkyl group having a chain

23 length of from 6 to 18 carbon atoms, more preferably 10 to 16 carbon atoms,

24 most preferably 12 to 16 carbon atoms, for example, 12 carbon atoms.

25

26 The surfactant is suitably present in the first base emulsion in an amount

27 ranging from 0.5 to 20% by weight, more preferably from 1 to 15% by weight,

28 and more preferably from 2 to 10% by weight.

29

30 **First Aqueous Phase Including Treatment Chemical**

31

32 The first aqueous phase may contain a number of components including

33 water, the treatment chemicals, and a solvent. In the preferred example, the

1   treatment chemical is a scale inhibitor such as an organic phosphonate.

2   Other treatment chemicals, by way of example, and not limitation, include

3   corrosion inhibitors, asphaltene inhibitors, gas hydrate inhibitors, wax

4   deposition inhibitors, and polymer and conformance controllers. Those

5   skilled in the art will appreciate that other treatment chemicals may also be

6   used in conjunction with other reactive chemicals which generally benefit

7   from remaining separated until being placed into a subterranean formation.

8

9   The volume fraction of the aqueous phase in the emulsion may be as high as

10   80%. In the first emulsion containing the scale inhibitor, the aqueous phase

11   may range from 1-80%, preferably 10 to 50%, more preferably 30 to 45%.

12

13   **Aqueous Phase**

14

15   The aqueous phase in the emulsion may comprise fresh water, sea water,

16   produced or formation water. The aqueous phase may have a total salinity of

17   0-250 g/l, for example 5-50 g/l. The aqueous phase may have a pH of 0.5-9.

18   Where the aqueous phase comprises a sea-water solution of a highly acidic

19   production chemical such as, for example, a scale inhibitor, the aqueous

20   phase may have a highly acidic pH, such as 0.1-5.

21

22   **Scale Inhibitor**

23

24   An oil field or gas field production scale inhibitor is effective in stopping

25   calcium and/or barium scale or other scales. The scale inhibitors may be a

26   water-soluble organic molecule with at least 2 carboxylic and/or phosphonic

27   acid and/or sulfonic acid groups e.g. 2-30 such groups. Examples of such

28   compounds used as inhibitors are aliphatic phosphonic acids with 2-50

29   carbons, such as hydroxyethyl diphosphonic acid, and aminoalkyl phosphonic

30   acids, e.g. polyaminomethylene phosphonates with 2-10 N atoms e.g. each

31   bearing at least one methylene phosphonic acid group; examples of the latter

32   are ethylenediamine tetra(methylene phosphonate), diethylenetramine

33   penta(methylene phosphonate) and the triamine- and tetramine-

1 polymethylene phosphonates with 2-4 methylene groups between each N
2 atom, at least 2 of the numbers of methylene groups in each phosphonate
3 being different (e.g. as described further in published EP-A479462, the
4 disclosure of which is herein incorporated by reference). Other exemplary
5 scale inhibitors are polycarboxylic acids such as acrylic, maleic, lactic or
6 tartaric acids, and polymeric anionic compounds such as polyvinyl sulphonic
7 acid and polyacrylic acids, optionally with at least some phosphonyl or
8 phosphinyl groups as in phosphinyl polyacrylates.
9
10 Table 1 below lists the most preferred scale inhibitors to be used in the first
11 aqueous phase.
12
13   TABLE 1
14

SYMBOL	CHEMICAL NAME
NTMP	Nitrilo tri(methylene phosphonic acid)
BHPMP	Bis-hexamethylene triamine-penta(methylene phosphonic) acid
PAA	Poly(acrylic) acid
DTPMP	Diethylene triamine-penta(methylene) phosphonic) acid
PPCA	Phosphinopolycarboxylic acid
SPA	Sulfonated polyacrylic acid
HEDP	1-Hydroxyethylidene-1,1-diphosphonic acid
HDTMP	Hexamethylene diamine-tetra(methylene phosphonic) acid

1   The amount of scale inhibitor used is preferably in the range from 1-50% w/w

2   of the aqueous phase, more preferably from 5-30% w/w, and most preferably

3   from 6-20% w/w. The amount of inhibitor used is dependent on the severity of

4   the scaling tendency, production rate of water, and the desired squeeze life.

5   The most preferred scale inhibitor is dependent upon conditions such as the

6   scale mineral being inhibited, the water chemistry and temperature. For

7   example, in the situation where calcite or calcium carbonate is to be

8   prevented, a preferred inhibitor is nitrilo-tri(methylene phosphonate). If

9   barium sulfonate is to be inhibited bis-hexamethylene triamine-

10   penta(methylene phosphonate or a polymeric inhibitor may be preferred.

11   Also, combinations of these scale inhibitors may also be used.

12

13   **Solvent**

14

15   The first aqueous phase may comprise a water miscible solvent such as

16   methanol, ethanol, n-propanol, iso-propanol, n-butanol, iso-butanol, tert-

17   butanol, butyl monoglycol ether, butyl diglycol ether, butyl triglycol ether,

18   ethylene glycol mono butyl ether and ethylene glycol. The solvent can help

19   break up surfactant structures that may make the system too viscous, speed

20   equilibrium, and adjust the over all phase behavior. It is believed that the

21   presence of a solvent of intermediate solubility in the aqueous phase and oil

22   phase assists in making a stable emulsion. The most preferred solvent may

23   be butanol, however the preferred type and amount is very dependent on the

24   surfactant used, and the nature of the oil and brine.

25

26   The volume fraction of the solvent in the aqueous phase is generally in the

27   range from 1-50%, more preferably 10 to 40%, and most preferably 20 to

28   30%. The same solvents as described above with respect to the first base

29   emulsion are preferably used in the second aqueous phase as well.

1 **B.   Second Base Emulsion Including Retention Enhancing Chemical**

2

3 The second base emulsion containing the retention enhancing chemical also

4 preferably has an oil continuous phase which is immiscible with a second

5 aqueous phase. The volume fraction of the aqueous phase in the second

6 emulsion is ideally the same as in the first aqueous phase, i.e., in the range

7 from 1-80%, preferably 10 to 50%, and more preferably from 30 to 45%. The

8 same oils may be used as was discussed above with respect to the emulsion

9 containing the first aqueous phase. Again, a surfactant is ideally used to

10 enhance the emulsification of the second base emulsion. The surfactant is

11 suitably present in the emulsion in an amount ranging from 0.5 to 20% by

12 weight, more preferably from 1 to 15% by weight, and most preferably from 2

13 to 10% by weight.

14

15 **Second Aqueous Phase Including Retention Enhancing Chemical**

16

17 The retention enhancing chemical, in the case where a scale inhibitor is used

18 in the first aqueous phase, is ideally a scale inhibitor precipitant. The

19 retention enhancing agent includes Group II metals, Group III metals, and

20 transition elements in an amount sufficient to react with the first treatment

21 chemical. The retention enhancing agents may include metal hydroxide,

22 metal oxide, metal alkoxide and mixtures thereof, and wherein the metal is

23 selected from the group comprising lithium, sodium, potassium, magnesium,

24 calcium, strontium, barium, boron or mixtures thereof. The retention

25 enhancing agent may also be chemicals which produce a retention favoring

26 pH when mixed with the inhibitor. Examples are simple mineral acids and

27 bases, organic acids, urea, and sulfamic acid. Organic molecules may also be

28 used as a retention enhancing chemical, particularly in the case of use with

29 conformance chemicals. Condensable aldehydes are an example. More

30 particularly, in the case of scale inhibitors, the most preferred retention

31 enhancing chemical contains calcium ion.

1 The molar ratio of scale inhibitor retention enhancing chemical to the scale
2 inhibitor is preferably between 0.5-20:1, more preferably from 10:1, and most
3 preferably about 2.5:1. The overabundance of retention enhancing chemicals
4 is especially valuable when the concentration of calcium or other retaining
5 chemical in the existing formation is non existent or low.
6
7 The volume fraction of the solvent in the aqueous phase in the overall
8 emulsion is generally in the range from 1-50%, more preferably 10 to 40%,
9 and most preferably 20 to 30%. The same solvents as described above with
10 respect to the first base emulsion are preferably used.
11
12 **II.   Introduction of the Emulsion into the Subterranean Formation**
13
14 The emulsion is introduced into the formation using the following steps.
15 Ideally, a pre-flush or spearhead is placed within the well bore and into the
16 formation. Ideally, this pre-flush has a hydrocarbon base. Next the emulsion
17 is delivered into the well bore and the formation to be treated. Next, a post
18 flush having a hydrocarbon base is used to squeeze or push the emulsion into
19 the formation. Ideally, an annular region of 4-12 feet around the well bore is
20 treated with the emulsion. The well bore and formation are then shut-in for a
21 period of 8-24 hours.
22
23 The oil continuous emulsion then ideally breaks or inverts from the oil
24 continuous phase to the water continuous phase. This allows treatment
25 chemical and retention enhancing chemical to react together causing the
26 treatment chemical to be retained by the rock in the formation. For the
27 purposes of this specification, the term "treatment chemical" which shall also
28 include reactants derived from the original treatment chemicals which react
29 with the retention enhancing chemical or agent which is then retained by the
30 formation and is used for treatment purposes. The emulsion ideally warms in
31 the reservoir and the emulsion phase behavior will shift becoming unstable.
32 The aqueous droplets from first and second aqueous phases will begin to
33 coalesce allowing the calcium and phoshonate to react and form a gel or

-13-

1   precipitation phase which falls out of solution and is retained on the formation

2   rock.

3

4   When the well is put back on production the oil phase and the aqueous

5   phase, minus the calcium and inhibitors retained in the formation, are

6   returned. Over the life of the squeeze, the inhibitor will be returned in the

7   production water from the formation at a low rate, but at a concentration that

8   is above the minimum concentration effective for preventing scale, for

9   example at a rate of 2-10 ppm. The life of the squeeze is over when the

10   return concentration of the inhibitor drops below the minimum effective

11   concentration.

12

13   The present invention increases the efficiency of the scale inhibitor by:

14

15   1.   extending the squeeze life;

16

17   2.   effectively placing the inhibitor in contact with the formation rock

18   by ideally forming an insoluble phase which precipitates or

19   adsorbs out of the aqueous phase or is otherwise retained by

20   the formation;

21

22   3.   increasing the retention time or amount of time the inhibitor is

23   effective by controlling the stoichiometry of the inhibitor to

24   retention enhancing chemical reaction; and

25

26   4.   decreasing the amount of unused, misplaced or returned

27   inhibitor.

28

29   While in the foregoing specification this invention has been described in

30   relation to certain preferred embodiments thereof, and many details have

31   been set forth for purpose of illustration, it will be apparent to those skilled in

32   the art that the invention is susceptible to alteration and that certain other

1   details described herein can vary considerably without departing from the

2   basic principles of the invention.